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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 04/11/2008 / Priority: 1. Chemistry / 2. JIS (Japan Industrial Standards) term / 3. Technical term

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1] Base Organic inorganic matter bipolar membrane which replaces a part of oxygen of the oxide of owner *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. for the oxide of the cation atom which can form oxide network covered by the surface of the base by an organic group It is the coating article equipped with the above, and said organic inorganic matter bipolar membrane is characterized by expressing an alkali metal oxide with the number of alkali metal atoms, and the total number sum total of said alkali metal atom and said cation atom containing it 0.1 to 30%.

[Claim 2] Said organic inorganic matter bipolar membrane is a coating article according to claim 1 with which an alkaline earth metal oxide is expressed with the number of alkaline earth metal atoms, and the total number sum total of said alkali metal atom, said alkaline earth metal atom, and said cation atom contains it 0.1 to 30% further.

[Claim 3] Said organic inorganic matter bipolar membrane is a coating article according to claim 1 or 2 which expresses said organic group with the number, and contains under double precision by 0.001 or more times of the total number sum total of said alkali metal atom, an alkaline earth metal atom, and said cation atom.

[Claim 4] Claim 1 whose 50 to 100% of the totals of said organic group are an alkyl group and/or a fluoro alkyl group - a coating article given in any 1 clause of three.

[Claim 5] The oxides of the cation atom which can form said oxide network are Claim 1 which is a silicon oxide - a coating article given in any 1 clause of four.

[Claim 6] Have an un-hydrolyzing nature organic group and (A) A hydrolysis and the organometallic compound in which condensation polymerization is possible, (B) An acid, the (C) alkali metal compound, and the constituent for covering that contains the compound in which hydrolyzed condensation polymerization is [ that condensation polymerization is completely possible or ] possible, and (D) (E) alkaline earth metal compound if needed,

respectively.

[Claim 7] The constituent for covering according to claim 6 which the number of the alkali metal atoms of the aforementioned (C) component contains 0.1 to 30% to the sum total of the number of the cation atoms except the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component.

[Claim 8] The constituent for covering according to claim 6 which the number of the cation atoms except the organic group of the aforementioned (D) component contains 0 to 99.8% to the sum total of the number of the cation atoms except the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component.

[Claim 9] The constituent for covering according to claim 6 which the number of the alkaline earth metal atoms of the aforementioned (E) component contains 0.1 to 30% to the sum total of the number of the cation atoms except the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component.

[Claim 10] As opposed to the sum total of the number of the cation atoms except the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component The number of the cation atoms except the organic group of the aforementioned (A) component 0.1 to 99.8%, [ the number of cation atoms excluding / the number of the alkali metal atoms of the aforementioned (C) component / the organic group of 0.1 - the 30% and the aforementioned (D) component ] The constituent for covering according to claim 6 with which the number of the alkaline earth metal atoms of 0 to 99.7% and the aforementioned (E) component contains 0.1 to 30%, respectively, and contains 0.001 - 3 regulation and water for the aforementioned (B) component zero to 5weight % further, respectively.

[Claim 11] As for said constituent for covering, the boiling points in an atmospheric pressure are Claim 6 containing a solvent of 150 degrees C or less - a constituent for covering given in any 1 clause of ten.

[Claim 12] Said solvent is a constituent for covering according to claim 11 which is an alcohol.

[Claim 13] The aforementioned (A) components are Claim 6 which is FUROORO alkyl-group content trialkoxysilane - a constituent for covering given in any 1 clause of 12.

[Claim 14] How to manufacture the coating article which applies Claim 6 - the constituent for covering given in any 1 clause of 13 to a base surface, and is characterized by drying.

[Claim 15] Said desiccation is the manufacture method of the coating article according to claim 14 performed at a room temperature.

[Claim 16] Said desiccation is the manufacture method of the coating article according to claim 14 or 15 performed in the atmosphere of 40% or less of relative humidity.

[Claim 17] The manufacture method of Claim 14 which heats at the temperature of 300

degrees C or less after said desiccation still more highly than a room temperature - a coating article given in any 1 clause of 16.

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#### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture method of the organic inorganic matter bipolar membrane coating article formed in the base surface of glass, Ceramics Sub-Division, plastics, or a metal, the constituent for organic inorganic matter bipolar membrane covering, and an organic inorganic matter bipolar membrane coating article.

[0002]

[Description of the Prior Art] The technology which reforms the surface of a base material is known by preparing the organic inorganic matter bipolar membrane which has an inorganic acid ghost and an organic group in the surface of a glass plate and other base materials.

[0003] The solution which mixed silicon alkoxide, the displacement silicon alkoxide by which a part of alkoxyl group was replaced by the fluoro alkyl group, an alcohol, water, and an acid (or base) in JP,H4-338137,A is applied to the glass substrate surface, and is calcinated. The glass with which the organic inorganic matter bipolar membrane which has water repellence was covered is indicated.

[0004] The organic inorganic matter bipolar membrane coating article which has the water repellence processed with the solvent and the constituent which dissolves in a nonaqueous system solvent preferably in the mixture of perfluoro-alkyl alkyl silane and Silang (for example, tetra-chlorosilane) which can be hydrolyzed completely is indicated by JP,H8-239653,A.

[0005] The organic inorganic matter bipolar membrane coating article which has the water repellence processed with the constituent which dissolves a chlorosilyl machine content compound and a fluoro alkyl-group content silane compound in alcoholic solvent is indicated by JP,H11-71682,A.

[0006]

[Problem(s) to be Solved by the Invention] The organic inorganic matter bipolar membrane in such technology applies to a base material the solution containing the silane compound which has the silane compound and the water-repellent machine which can be hydrolyzed, and is produced by what is called sol gel process to dry. In a sol gel process, since volatilization of a solvent advances in parallel with formation of oxide binding, in desiccation of 400 degrees C or less, a detailed pore exists in a film, and membranous hardness is not high. In order to make this nonporous and to raise membranous hardness, calcination at 500-600 degrees C is indispensable, but at such a temperature, an organic group like a water-repellent machine which contributes to surface treatment will decompose. Therefore, in said technology,

membranous desiccation or membranous hardening was performed at the temperature of 250 degrees C or less, and the obtained organic inorganic matter bipolar membrane did not turn into a film which has high hardness like the oxide obtained with scorification, or Ceramics Sub-Division, for example, although the oxide was a principal component.

[0007] When such an organic inorganic matter bipolar membrane coating article is used outdoors, for example, the characteristics by which the crack was easily attached to the membrane surface, as a result reforming was carried out will be lost by being put to the situation where sand is sprayed. Moreover, in order to remove dust, the adhering mud, or adhering sand, a film will get damaged and separate also by wiping the surface with cloth etc. Furthermore, even when dust etc. has not adhered, by friction (for example, surface \*\*\*\* of the windowpane of a car with a wiper etc.) with cloth, a brush, etc. which consist of hard fiber, a small crack will be formed and deterioration of characteristics will be promoted.

[0008] This invention is made in view of the above problems. The purpose is to offer the coating liquid composition for the method of manufacturing the goods with which the organic inorganic matter bipolar membrane which is equal also to outdoor use, and which has high hardness and has water repellence and other functionality was covered, and this coating article for the outstanding productivity, and this coating article manufacture.

[0009]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, this invention persons discovered the hardness of organic inorganic matter bipolar membrane rose by leaps and bounds rather than having made organic inorganic matter bipolar membrane contain alkali metal ion.

[0010] That is, it is the coating article characterized by for said organic inorganic matter bipolar membrane expressing an alkali metal oxide with the number of alkali metal atoms in the coating article characterized by this invention possessing the following, and the total number sum total of said alkali metal atom and said cation atom containing 0.1 to 30%. Base Organic inorganic matter bipolar membrane which replaces a part of oxygen of the oxide of owner *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. for the oxide of the cation atom which can form oxide network covered by the surface of the base by an organic group

[0011] When forming an oxide film by a sol gel process generally, metal alkoxide, for example, alkoxide of silicon (Si), is used as a starting material in many cases. In a sol gel process, since volatilization of a solvent advances in parallel with formation of binding (siloxane bond) of the metal by a dehydration condensation reaction, for example, silicon, (Si), and oxygen (O), it becomes the porosity silica membrane to which a detailed pore exists in a film. Since binding of this silicon and oxygen is covalent bond nature and silicon and oxygen are combined with big bond energy, In the volatilization stage of a solvent if a siloxane bond forms three-dimensional structure to some extent Although a dehydration condensation reaction

progresses after that, contraction of that structure will be controlled, the portion into which the water generated at the alcohol and dehydration condensation reaction which were generated by the solvent and the hydrolysis reaction volatilized will remain as a pore, and a silanol group, an alkoxyl group, water, or an alcohol will exist in this pore. The hardness of this porosity silica membrane is not so high because of that porosity. When this film is heated at the temperature of 500 degrees C or more, a membranous pore disappears, serves as silica membrane of the quality of nonporous, and has high hardness. However, since a water-repellent organic group like a fluoro alkyl group is decomposed with this cooking temperature, for example, at the temperature (for example, 300 degrees C or less) which a water-repellent organic group does not decompose [ membranous cooking temperature ], a membranous pore hardly disappears and membranous hardness does not become high.

[0012] In this invention, an alkali metal oxide is introduced into organic inorganic matter bipolar membrane. Since ion character of an alkali metal is strong, it exists in the state of an ion in a solution also in the volatilization stage of a solvent by making it dissolve into the coating liquid for film formation, and making it coexist with the metallic compounds (for example, silane compound) in which a hydrolysis like silicon alkoxide is possible. Since an alkali metal (M) ion is univalent, it reacts with metal hydroxyl (for example, silanol group). A metal forms for example, "O-+M" binding as compared with binding of "Si-O-Si" which combines with oxygen (O) as finally shown in the following formula (1) inside a film and whose directivity of binding is more nearly free when it is silicon (Si). Therefore, the frame of the organic inorganic matter bipolar membrane which introduced the alkali metal oxide is [ become ] easy to change with heat as compared with the frame of the film which does not contain an alkali metal oxide. As a result, according to this invention, a frame changes with desiccation or heating of a temperature lower than the decomposition temperature (250-300 degrees C) of the organic group contained in organic inorganic matter bipolar membrane, many pores disappear, a film elaborates, and a film with very high hardness is obtained.

[Formula 1]

**\*\*Si-O-+M (M is an alkali metal) (1)**

[0013] The organic inorganic matter bipolar membrane in this invention can be made to contain an alkaline earth metal oxide. Ion character of an alkaline earth metal is strong like an alkali metal. Membranous abrasion resistance can be raised further, without spoiling the cold cure characteristics by alkali metal introduction by making an alkaline earth metal oxide contain. Although the organic inorganic matter bipolar membrane in this invention contains the organic group like the after-mentioned, this organic group exists by the density higher than the inside of organic inorganic matter bipolar membrane on the surface. Addition of an alkaline earth metal oxide can raise the density of the membrane surface of this organic group further, and, as a result, the function of an organic group can be raised further. For example, when an

organic group is a water-repellent machine, a membranous contact angle is made still higher by addition of an alkaline earth metal oxide, waterdrop can roll and a sex can be made still better.

[0014] In this invention although lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr) are used as said alkali metal Li and Cs are suitably used for the Reason for that acquisition is easy in these, and the solubility to both water and an alcohol being high. Moreover, although calcium (Ca), magnesium (Mg), strontium (Sr), barium (Ba), radium (Ra), and beryllium (Be) are used as said alkaline earth metal Ca and Mg are suitably used for the Reasons of there not being that acquisition is easy, the solubility to both water and an alcohol being high, and toxicity in these.

[0015] Since a segregation will be carried out, it will become heterogeneous and membranous hardness will fall, if too conversely large [ if there is not much little content of the alkali metal oxide in organic inorganic matter bipolar membrane, the effect of cold cure nature will not be acquired, and ] This content is 0.1 to 30% of the total of the total number sum total of the cation atom which constitutes the oxide which expresses with the number of alkali metal atoms, and forms the network of organic inorganic matter bipolar membrane, an alkali metal atom, and said below-mentioned alkaline earth metal atom, and is 1 to 25% preferably.

[0016] Since a segregation will be carried out, it will become heterogeneous and membranous hardness will fall if there is too much content of the alkaline earth metal oxide in organic inorganic matter bipolar membrane, [ such content ] The cation atom which expresses with the number of alkaline earth metal atoms, and constitutes the network formation inorganic acid ghost of organic inorganic matter bipolar membrane, It is desirable that it is 0 to 30% of the total number sum total of said alkali metal atom and said alkaline earth metal atom, it is more desirable that it is 0.1 to 30%, and it is still more desirable that it is 1 to 25%. [ however, the sum total of the content of an alkali metal oxide and an alkaline earth metal oxide ] It expresses with the sum total number of said alkali metal atom and an alkaline earth metal atom, and it is desirable that it is 50% or less of the total number sum total of said cation atom, said alkali metal atom, and said alkaline earth metal atom.

[0017] The organic inorganic matter bipolar membrane in this invention has the oxide of the cation atom which can form oxide network. As this cation atom, silicon, titanium, zirconium, an aluminium, germanium, a tantalum, tin, antimony, cerium, lanthanum, tungsten, indium, boron, etc. can be raised. In these, it is comparatively hard to produce a condensation thing and a crystal during membrane formation, and since a film without a crack is easy to be obtained, silicon is used preferably.

[0018] The organic inorganic matter bipolar membrane in this invention has the oxide of the cation atom which can form oxide network, and a part of oxygen of the oxide is replaced by the organic group. Although it does not limit especially as this organic group, a univalent organic

group is desirable. for example, [ alkyl groups, such as a methyl group, an ethyl group, and an isopropyl group, a phenyl group, a vinyl group, an aminopropyl machine, an acrylic machine, an epoxy group, a polyether machine, and a pan ] All the all [ a part or ] of a hydrocarbon can mention a fluoro alkyl group, a chloro alkyl group, etc. which were replaced by fluorine or chlorine. In these, an alkyl group and the fluoro alkyl group can give water repellence to a film, the methyl group can give low friction nature to a film, and an aminopropyl machine and the polyether machine can give hydrophilicity to the surface, for example.

[0019] These organic groups exist in the form combined with the cation atom (example; silicon atom) of the inorganic acid ghost (for example,  $\text{SiO}_2$ ) which forms the network in organic inorganic matter bipolar membrane. Since membranous hardness will decrease if too conversely large [ if the content of this organic group is too small not much, it will not contribute to reforming of a base surface and a film will not exhibit a predetermined function, and ] It is desirable that it is under double precision in 0.001 or more times of the total number sum total of the cation atom of the inorganic acid ghost which expresses with the number of an organic group and forms the network in organic inorganic matter bipolar membrane, said alkali metal atom, and an alkaline earth metal atom. They are 0.01 time - 1 time more preferably. Although this organic group may be uniformly distributed in the membranous thickness direction, even if it serves as an inclination presentation film to which that concentration changes from the interface side with a base toward the outside surface, it is not cared about. For example, in order to give a water-repellent function, when the alkyl group and/or fluoro alkyl group in a film are made to contain so that the number may turn into 50 to 100% of the total number of an organic group, film hardness and an interval serve as a water-repellent membrane with high durable performance, and are still more desirable.

[0020] By this invention, thus, alkali metal ion, Or by including alkali metal ion and an alkaline earth metal ion, also with the desiccation or heating below the decomposition temperature of the organic group which contributes to surface treatment, the film which has the high hardness which was not obtained conventionally was obtained, and, as a result, the durable performance of organic inorganic matter bipolar membrane improved by leaps and bounds.

[0021] In addition to the reforming characteristics by an organic group, such cold cure nature is not checked, for example, even when controlling a membranous refractive index or introducing a transition metal ion etc. further into a film for the purpose of adding further the function which controls visible light transmittance. Namely, by making the metal ion and alkali metal oxide (or both the alkali metal oxide and the alkaline earth metal oxide) which discover the target function live together [ with desiccation or heating of 300 degrees C or less of temperature ] Hardness is very high and it can be considered as the compound functional film having the function by the reforming characteristics by an organic group, and a metal ion. For example, the organic inorganic matter bipolar membrane colored by adding cobalt oxide, iron oxide,

nickel oxide, and copper oxide can be obtained.

[0022] Moreover, although it is possible to make it contain like said bipolar membrane also about organic molecules, such as organic coloring matter, as for the organic molecule except being contained as said organic group, it is desirable to carry out to 5 or less weight % to film weight. It is because cold cure ability may be spoiled if it adds exceeding this.

[0023] If membranous thickness is too large not much, film hardness will fall easily, and if too not much small, the effect of surface treatment will not be acquired. Therefore, 5-200nm of thickness [ 5-100nm of ] is 5-50nm still more preferably more preferably.

[0024] Moreover, the organometallic compound with which this invention has (A) unhydrolyzing nature organic group, (B) They are an acid, the (C) alkali metal compound, and the constituent for covering that contains the compound in which condensation polymerization is completely possible, and in which \*\*\*\*\* is possible again, and (D) (E) alkaline earth metal compound if needed, respectively.

[0025] As for the aforementioned (A) component, the number of the cation atoms except the organic group is the sum total (however, except for the cation atom in an organic group) of the number of the cation atoms of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component. the following -- being the same -- containing is desirable so that it may receive and may become 0.1 to 99.8%, and it is more desirable to contain so that it may become 1.0 to 90%. As opposed to the sum total of the number of cation atoms excluding [ the number of the alkali metal atoms ] the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component in the aforementioned (C) component Containing is desirable so that it may become 0.1 to 30%, and it is more desirable to contain so that it may become 1 to 25%. The aforementioned (D) component is a component which strengthens binding with a film and a substrate more. (D) As for a component, it is desirable to contain so that the number of the cation atoms except the organic group may become 0 to 99.7% to the sum total of the number of the cation atoms except the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component, and containing 1 to 88% is more desirable. And the aforementioned (E) component receives the sum total of the number of cation atoms excluding [ the number of the alkali metal atoms ] the organic group of the aforementioned (A) component, the (C) component, the (D) component, and the (E) component. Containing is desirable so that it may become 0.1 to 30%, and it is more desirable to contain so that it may become 1 to 25%.

[0026] Although the (D) component in this invention is not an essential ingredient, it is possible for you to make it dissolve in the alcohol which is a common solvent as a (D) component, and the compound in which a hydrolysis and condensation polymerization are completely possible, or the compound in which condensation polymerization is completely possible can use it

extensively. The compound in which a hydrolysis and condensation polymerization are completely possible is a compound which the hydrolysis nature machine combined with the cation atom, and is a compound with the number equal to the valence of a cation atom of hydrolysis nature machines. Moreover, the compound in which condensation polymerization is completely possible is a compound which the hydroxyl group combined with the cation atom, and is a compound with the number equal to the valence of a cation atom of hydroxyl groups. (D) the cation atom (silicon --) which can form oxide network as a component, for example Alkoxide, such as titanium, zirconium, an aluminium, germanium, a tantalum, gallium, tin, antimony, cerium, lanthanum, tungsten, indium, scandium, yttrium, and boron, a hydroxide, a chloride, nitrate, etc. can be mentioned. What is necessary is to carry out chelating by beta diketones, such as acetylacetone, etc., and just to add like alkoxide, such as titanium, zirconium, an aluminium, and boron, when a solution with it is hard to be obtained. [ very high reactivity and ] [ homogeneous in addition of only this ] In the case of a compound which melts into water although it does not melt into an alcohol, you may add water if needed. As a component, more specifically (D) Silicon tetra-alkoxide, such as tetramethoxy silane and tetraethoxy silane, Titanium tetra-alkoxide, such as titanium tetraisopropoxide and titanium tetrabutoxide, Zirconium tetra-isopropoxide, zirconium tetra-ethoxide, Zirconium tetra-alkoxide, such as zirconium tetra-butoxide,  $H_3BO_3$ ,  $ZrOCl_2$ , and  $ZrO(NO_3)_2$ ,  $AlCl_3$ ,  $GeCl_4$ ,  $TaCl_5$ ,  $GaCl_3$ ,  $InCl_3$ ,  $ScCl_3$ ,  $YCl_3$ ,  $LaCl_3$ ,  $CeCl_3$ , aluminum( $NO_3$ )<sub>3</sub>,  $Ga(NO_3)_3$ ,  $In(NO_3)_3$ ,  $SbCl_3$ ,  $WCl_6$ ,  $Sc(NO_3)_3$ ,  $Y(NO_3)_3$  Solubility [ as opposed to water or an alcohol in the compound of 3,  $La(NO_3)_3$ , and  $Ce(NO_3)_3$  grade ] can use it conveniently highly.

[0027] As an alkali metal compound which is the aforementioned (C) component, it is possible for you to make it dissolve in an alcohol, for example, the chloride of an alkali metal (lithium, sodium, potassium, rubidium, caesium, francium), nitrate, etc. are used. More specifically, solubility [ as opposed to water or an alcohol in metallic compounds, such as  $LiCl$ ,  $NaCl$ ,  $KCl$ ,  $RbCl$ ,  $CsCl$ , and  $FrCl$ , ] can use it conveniently highly.

[0028] Although the alkaline earth metal compound which is the aforementioned (E) component is not an essential ingredient, as a (E) component It is possible for you to make it dissolve in an alcohol, for example, the chloride of an alkaline earth metal (beryllium, magnesium, calcium, strontium, barium, radium), nitrate, etc. are used. More specifically, solubility [ as opposed to water or an alcohol in the metallic compounds of  $BeCl_2$ ,  $MgCl_2$ ,  $Mg(NO_3)_2$ ,  $CaCl_2$ ,  $Ca(NO_3)_2$ ,  $SrCl_2$ ,  $BaCl_2$ ,  $RaCl_2$ , and  $Ba(NO_3)_2$  grade ] can use it conveniently highly.

[0029] As an organometallic compound which has the un-hydrolyzing nature organic group in this invention which is the (A) component For example, the metallic compounds of the compounds indicated as the aforementioned (D) component, That is, the compound with which a part of anion of the compound of silicon, titanium, zirconium, an aluminium, germanium, a

tantalum, tin, antimony, cerium, lanthanum, tungsten, and indium was replaced by the organic group of un-hydrolyzing nature can use it conveniently. Each of these metals is the cation atoms which can form oxide network. Although it does not limit especially as an organic group of un-hydrolyzing nature, a methyl group, Alkyl groups, such as an ethyl group and an isopropyl group, a phenyl group, a vinyl group, an aminopropyl machine, an acrylic machine, an epoxy group, the fluoro alkyl group by which all the all [ a part or ] of the hydrocarbon was replaced further, a chloro alkyl group, etc. are mentioned. These organic groups remain in organic inorganic matter bipolar membrane, and give functionality, such as water repellence, low friction nature, and hydrophilicity, to a film. Since the organic silicon compound which has such a nondegradable organic group is obtained as a comparatively stable compound, it can be used especially preferably.

[0030] for example, as a silane compound which has an alkyl group  $\text{CH}_3(\text{CH}_2)_{18}\text{SiCl}_3$ ,  $\text{CH}_3(\text{CH}_2)_{16}\text{SiCl}_3$ ,  $\text{CH}_3(\text{CH}_2)_2\text{SiCl}_3$ ,  $\text{CH}_3\text{CH}_2\text{SiCl}_3$ ,  $2(\text{CH}_3\text{CH}_2)\text{SiCl}_2$ ,  $3(\text{CH}_3\text{CH}_2)\text{SiCl}$ ,  $\text{CH}_3\text{SiCl}_3$ ,  $2\text{SiCl}_2$ ,  $(\text{CH}_3)$  Alkyl-group content chlorosilane;  $\text{CH}_3(\text{CH}_2)_{18}\text{Si}(\text{OCH}_3)_3$  like  $3\text{SiCl}$ ,  $\text{CH}_3(\text{CH}_2)_{16}\text{Si}(\text{OCH}_3)_3$ ,  $\text{CH}_3(\text{CH}_2)_8\text{Si}(\text{OCH}_3)_3$ ,  $\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OCH}_3)_3$ ,  $\text{CH}_3(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3$ ,  $\text{CH}_3\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  $(\text{OCH}_3)_2\text{Si}(\text{CH}_3\text{CH}_2)_2$ ,  $(\text{OCH}_3)_3\text{SiOCH}_3$ ,  $\text{CH}_3\text{Si}(\text{CH}_3\text{CH}_2)_3$ ,  $(\text{OCH}_3)_2\text{Si}(\text{CH}_3)_2$ ,  $(\text{OCH}_3)_3\text{SiOCH}_3$ ,  $\text{CH}_3(\text{CH}_3)_{18}\text{Si}(\text{CH}_2)_3$ ,  $\text{CH}_3(\text{OC}_2\text{H}_5)(\text{CH}_2)_{16}\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $\text{CH}_3(\text{CH}_2)_8\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $\text{CH}_3(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $\text{CH}_3\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $2(\text{CH}_3\text{CH}_2)\text{Si}(\text{OC}_2\text{H}_5)_2$ , Alkyl-group content alkoxysilane like  $3\text{SiOC}_2\text{H}_5$ ,  $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $2(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$ , and  $3(\text{CH}_3)\text{SiOC}_2\text{H}_5$ ,  $(\text{CH}_3\text{CH}_2)\text{CH}_3\text{O}(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$  -- ( -- here -- n -- end methoxyl poly dimethylsiloxane like 2 - 2000), and  $\text{HO}(\text{Si}(\text{CH}_3)_2\text{O})_n\text{H}$  -- ( -- as for n, end silanol poly dimethylsiloxane like 2 - 2000) etc. is mentioned here.

[0031] moreover, as a silane compound which has a FUROORO alkyl group  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SiCl}_3$ ,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ ,  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ ,  $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{SiCl}_3$ , and  $\text{CF}_3\text{CF}_2(\text{CH}_2)_2\text{SiCl}_3$ ,  $\text{CF}_3$  FUROORO alkyl-group content trichlorosilane;  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$  like  $2\text{SiCl}_3$ ,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ , and  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{CH}_2)(\text{OCH}_3)_3$ ,  $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ,  $\text{CF}_3\text{CF}_2(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ,  $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ , and \*\* -- FUROORO alkyl-group content trialkoxysilane [ like ] is mentioned.

[0032] Although a water-repellent function can be given to the base material surface by using these FUROORO alkyl-group content silane compound It can be considered as the film which combines the outstanding water-repellent performance and the durable performance by using trichlorosilane, trialkoxysilane, etc. containing the FUROORO alkyl group which has ten or more fluorine atoms. especially --  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$  (heptadecafluorodecyl trimethoxysilane ) -- and --  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$  (heptadeca fluoro decyltrichlorosilane) It can be used preferably.

[0033] Although it is not limited, since especially the acid that is the (B) component in the

constituent for covering in this invention can be used as a film with high hardness as what evaporates during desiccation and cannot remain in a film easily, it is desirable. For example, hydrochloric acid, nitric acid, acetic acid, fluoric acid, formic acid, trifluoroacetic acid, etc. are mentioned. Especially, also when having and dealing with a high degree of electrolytic dissociation and volatility, especially comparatively safe hydrochloric acid is desirable. As for the aforementioned (B) component, it is desirable that 0.001-3 regulation content is carried out.

[0034] In the boiling point in an atmospheric pressure, as a solvent in this invention, a solvent of 150 degrees C or less can use it extensively. For example, hexane, toluene, a hydrocarbon like cyclohexane, methyl chloride, Carbon tetrachloride, halogenated hydrocarbon like trichloroethylene, acetone, ketone like methyl ethyl ketone, a nitrogen-containing compound like diethylamine, ester like ethyl acetate, and alcohols can be used. Although alcoholic solvent is used preferably, for example, methanol, ethanol, 1-propanol, 2-propanol, butyl alcohol, amyl alcohol, etc. can be mentioned also in these Since the vapor rate [ in / carbon number / like methanol, ethanol, 1-propanol, and 2-propanol / in three or less chain type saturation monohydric alcohol / ordinary temperature ] is large in them, it is used still more preferably.

[0035] Said alcohol may contain 0 weight % or more and 50weight % or less of water. Although 0.2weight % or more of moisture is usually contained in the commercial best alcohol, in this invention, it can use preferably, without carrying out treatment which leads to the cost rise of dehydration treatment etc. Moreover, when adding a metallic raw material, beforehand, metallic compounds may be dissolved in water and it may add, or in order to control a rate of drying and the viscosity of liquid, you may add others and a solvent. It is desirable that the carbon number mentioned above also on that occasion is [ the quantity of three or less chain type saturation monohydric alcohol ] 10 weight % or more to the amount of solvents. A homogeneous and transparent film may not be obtained in the quantity not more than this.

[0036] In the constituent for covering (coating solution) containing the - (E) component (aforementioned [ A ]), as for the aforementioned (A) component and the (D) component, a hydrolysis reaction and a dehydration condensation reaction advance with the water of some in a catalyst (B) component and a solvent. If a lot of water exists in coating liquid, the hydrolysis reaction of the above (A) and the (D) component and a dehydration condensation reaction will be promoted, and the pot life of coating liquid will become short, and it will become easy to produce the nonuniformity of thickness in the case of desiccation after spreading of KOTEINGU liquid. Therefore, in order to lengthen the pot life of a solution and to lose the nonuniformity of the thickness in the case of desiccation after spreading, the smaller possible one of the concentration of the water in a coating solution is desirable. setting to this invention, since 0.2weight % or more of moisture is usually contained in the commercial alcohol -- this moisture -- although it comes out enough, when adding water separately, as for the

concentration of the water in coating liquid, it is desirable that it is 0 to 5 weight %, and it is still more desirable that it is 0 to 2 weight %. Even if the concentration of the water in coating liquid is zero, since the moisture in the air is absorbed by the spreading film after being applied to the base material, a hydrolysis reaction is not checked.

[0037] [ the method ] although the coating method in particular in this invention is not limited For example, dip coating, flow coating, curtain coating, spin coating, spray coating, bar coating, roll coating, brush coating coating, etc. can be illustrated.

[0038] Spreading in this invention is performed by 0-40 degrees C, for example, a room temperature, in the atmosphere of 40% or less of relative humidity. Desiccation after spreading is performed by 0-40 degrees C, for example, a room temperature, for [ 10 seconds - ] 20 minutes in the atmosphere of 40% or less of relative humidity. You may heat for [ for / 30 seconds / - ] 10 minutes at the temperature of 300 degrees C or less if needed more highly than a room temperature after that. Therefore, the film of high hardness which has functionality peculiar to an organic group can be obtained, without the organic group which constitutes a film decomposing. When the organic group of functionality is a water-repellent machine and it heats in temperature of 300 degrees C or less after the above-mentioned spreading more highly than a room temperature, it is desirable that \*\*\*\*\* of the film obtained performs desiccation at a room temperature after spreading since \*\*\*\* and resistance to UV rays fall easily.

[0039] As a base material in this invention, the thing of the form of transparent or opaque plates, such as glass, Ceramics Sub-Division, plastics, or a metal, a rod-like structure, and other versatility is mentioned. [ on the surface of a base material, when there are few hydrophilic radicals, process and hydrophilicity-ize the surface in the plasma or the Corona atmosphere which contains oxygen beforehand, or ] Or after irradiating the ultraviolet radiation of the wavelength near 200-300nm in the atmosphere which includes the base material surface for oxygen and performing hydrophilic-ized treatment, it is desirable to perform a surface treatment.

[0040]

[Embodiment of the Invention] A work example is raised to below and the form of operation of this invention is concretely explained to it.

[a work example 1] -- heptadecafluorodecyl trimethoxysilane ( $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ) and the product made from Shin-etsu silicone --) it may be called the following "FAS" -- 0.2g and tetra-ethoxy silane ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ) and the product made from Shin-etsu silicone --) It is ethanol (0.35 weight % of content moisture contents) about 0.6g, 0.00947g of lithium chloride, and 2g of concentrated hydrochloric acid (35 weight %) which may be called following "TEOS". Added agitating to 999.19 g, FAS and TEOS were made to hydrolyze, and coating liquid was obtained. Those total quantities are made into 100mol % for the content of FAS and TEOS

which are the metallic compounds in coating liquid, and lithium chloride, and molar fraction is shown in Table 1. [ this coating liquid ] on the surface of the glass substrate (3.4mm x 150x150mm) of the washed soda lime silicate glass composition It applied by the flow coat method at 30% of relative humidity, and a room temperature (20 degrees C), and the organic inorganic matter bipolar membrane covering glass plate which made the water-repellent membrane about 40nm thick cover was obtained by making it dry for about 1 minute at 30% of relative humidity, and a room temperature (20 degrees C). The molar fraction of the alkali metal atom to the sum total of the cation atom (silicon) which constitutes the inorganic acid ghost of the obtained organic inorganic matter bipolar membrane, and an alkali metal atom (lithium) was as being shown in Table 1.

[0041] About the organic inorganic matter bipolar membrane covering glass plate which has the obtained water-repellent function, the contact angle of water was measured as a static contact angle by waterdrop with a weight of 2mg using the contact angle meter (CA-DT, product made from Kyowa Interface Science). It means that static water repellence is excellent, so that the value of this contact angle is large. moreover, as a measure which shows the performance (waterdrop rolling sex) for which waterdrop rolls the surface of the covering glass plate which has water repellence Put the waterdrop of 50microl on the surface of the covering glass plate arranged horizontally, the glass plate was made to incline gradually, and the angle of gradient (critical angle of inclination) of the glass plate in case the waterdrop put on the surface begins to roll was measured. It means that the raindrop which the dynamic water-repellent performance is excellent in, for example, adhered to the windshield window of the car under run disperses easily, and a driver's field of view is not barred, so that a critical angle of inclination is small.

[0042] Furthermore, evaluation of membranous hardness was performed by measuring the static contact angle by waterdrop with a weight of 2mg which performed wear 100 times and carried out point \*\* by the 250g load to an organic inorganic matter bipolar membrane covering glass plate using the commercial Taber abrasion test.

[0043] The contact angle of the organic inorganic matter bipolar membrane film which has a water-repellent function, and the contact angle before and behind the Taber abrasion test are shown in Table 2. It was a film with a reduction the contact angle after the Taber examination is before and after the Taber examination, and small [ the contact angle before the Taber examination is as large as 108 degrees, and / a contact angle / are 90 degrees and ] about the obtained film, in a contact angle, and very high film hardness. Moreover, \*\*\*\*\* expressed \*\*\*\* with the critical angle of inclination, and was 8 times.

[0044] [Work examples 2-10] The organic inorganic matter bipolar membrane covering glass which has a water-repellent function like a work example 1 was obtained except having changed the raw material in the coating liquid of a work example 1 and component ratio of

metallic compounds, respectively, as shown in Table 1. The range of the thickness of organic inorganic matter bipolar membrane of all of work examples 2-10 was 5-50nm. The molar fraction of the alkali metal atom to the sum total of the presentation of the cation of the obtained film, i.e., the cation atom which constitutes the inorganic acid ghost network of organic inorganic matter bipolar membrane, an alkali metal atom, and an alkaline earth metal atom, or the alkaline earth metal atom was as being shown in Table 1. The result measured like the work example 1 is shown in Table 2.

[0045] The contact angle before the Taber examination of each obtained film was large, and the fall of the contact angle after the Taber examination was a small film with high hardness. When the work example 3 which does not contain an alkaline earth metal oxide is compared with the work example 4 which replaced some alkali metal oxides of the work example 3 with the alkaline earth metal oxide, it turns out that abrasion resistance and waterdrop roll [ the direction of a work example 4 ] as compared with a work example 3, and the sex is excellent.

[0046] [Comparative examples 1-5] The organic inorganic matter bipolar membrane covering glass which has a water-repellent function like a work example 1 was obtained except having changed the raw material in the coating liquid of a work example 1 and the amount of addition of metallic compounds, respectively, as shown in Table 1. The presentation of the cation of the obtained film was as being shown in Table 1. The result measured like the work example 1 is shown in Table 2.

[0047] The obtained film had the large fall of the contact angle after the Taber examination, although the contact angle before the Taber examination was large, the water-repellent performance was almost lost and film hardness was very low.

[0048] [a work example 11] -- as the metallic compounds which have a nonresponsive organic group in the coating liquid of a work example 1 -- end silanol poly dimethylsiloxane (the product made from Gelest --) The average molecular weight 4200 was used and the organic inorganic matter bipolar membrane covering glass which has a low friction function like a work example 1 was obtained except having changed the raw material and its amount of addition of metallic compounds, respectively, as shown in Table 1. However, a component ratio and each molar fraction express the content of end silanol poly dimethylsiloxane (average molecular weight 4200) with the number of moles converted into SiO<sub>2</sub>. The presentation of the cation of the obtained film was as being shown in Table 1.

[0049] Moreover, when the dynamic friction coefficient of paper and a film surface was measured using the surface measurement machine made from new east science "HEIDON-14", as for the coefficient of friction, it turned out that the 0.1 or less surface where frictional resistance is very small is obtained. As the obtained film was shown in Table 2, the contact angle before the Taber examination was large, and the fall of the contact angle after the Taber examination was a small film with high hardness. Moreover, when the coefficient of friction was

measured after the Taber examination, the coefficient of friction was 0.1 or less very small value like Taber examination before.

[0050] [Comparative example 6] Both the amount of LiCl used in the coating liquid of a work example 9 and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  used was made into zero, and the organic inorganic matter bipolar membrane covering glass which has a low friction function like a work example 9 was obtained except having changed DMS and TEOS, as shown in Table 1. The obtained film had the large fall of the contact angle after the Taber examination, although the contact angle before the Taber examination was large, the water-repellent performance was almost lost and film hardness was very low.

[0051] Moreover, like the work example 9, when the dynamic friction coefficient of the film surface was measured with Kami before the Taber examination and after the Taber examination, although, as for the coefficient of friction before the Taber examination, the 0.1 or less surface where frictional resistance is very small was obtained, the coefficient of friction after the Taber examination rose to 0.5.

[0052]

[Table 1]

-----	Metallic-compounds raw material component ratio	alkali metal
Alkaline earth metal (molar ratio)	Seed Content	Seed Content (mole %)
-----	Work example 1	FAS/TEOS/LiCl10/83/7Li7-02
FAS/TEOS/CsCl5/87/8Cs8-03	FAS/TEOS/LiCl10/80/10Li 10-04	FAS/TEOS/LiCl/MgCl <sub>2</sub> ·6H <sub>2</sub> O 10/80/7/3 Li7Mg35
FAS/LiCl/CaCl <sub>2</sub> ·2H <sub>2</sub> O98/1/1Li1Ca16	FAS/CsCl/MgCl <sub>2</sub> ·6H <sub>2</sub> O50/25/25 Cs 25 Mg 257	FAS/TEOS/CsCl/CaCl <sub>2</sub> ·6H <sub>2</sub> O 10/88/1/1 Cs 1 Ca 18
FAS/ZrOCl <sub>2</sub> ·8H <sub>2</sub> O/KCl10/80/10K 10-09	FAS/H <sub>3</sub> BO <sub>3</sub> /NaCl/CaCl <sub>2</sub> ·2H <sub>2</sub> O 50/40/5/5 Na 5Ca510	FAS/LiCl95/5Li 5-011
DMS/TEOS/LiCl/MgCl <sub>2</sub> ·6H <sub>2</sub> O1/89/7/3Li 7Mg3	Comparative Example 1	FAS100-0-02
FAS/TEOS10/90- 0 - 03	FAS/TEOS/LiCl 10/50/40 Li 40 - 04	FAS/TEOS/CsCl/MgCl <sub>2</sub> ·6H <sub>2</sub> O 5/15/40/40 Cs 40Mg 405
FAS/TEOS/CaCl <sub>2</sub> ·6H <sub>2</sub> O10/80/10-0Ca 106	DMS/TEOS1/99-0- 0-----*FAS:F(CF <sub>2</sub> ) <sub>8</sub> (CH <sub>2</sub> ) <sub>2</sub> Si(OC(CH <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub> , TEOS:Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , DMS: End silanol poly dimethylsiloxane (average molecular weight 4,200)	

[0053]

[Table 2]

-----	Abrasion test enclitic antenna (degree)	Contact angle after an abrasion test (degree)	Critical angle of inclination (degree)
-----	Work-example 1	108908	work-example 2108957
work-example 3108856	work-example 4108894	work-example 5108916	work-example 6108966
work-example 710898	Five work examples 8 108 92	Eight work examples 9 108 90	8 work-example 10107889
work-example 11100884	comparative-example 11086010	comparative-example	

2108739 comparative-example 31087510 comparative-example 41087812 comparative  
example 510876 13 comparative examples 6 100 78 10----- [0054]

[Effect of the Invention] As explained above, according to this invention, hardness can consider it as the organic inorganic matter bipolar membrane which improved by leaps and bounds by making organic inorganic matter bipolar membrane contain alkali metal ion. Moreover, while raising membranous hardness further by making an alkaline earth metal ion contain with alkali metal ion, the functionality of an organic group can be raised further.

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[Translation done.]